

ENHANCED DURABILITY OF HIGH-TEMPERATURE DESULFURIZATION SORBENTS FOR MOVING-BED APPLICATIONS

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1. - INTRODUCTION

Sulfur removal will be mandatory for all power generation coal gas applications in order to comply with future environmental standards. Two promising technologies that are currently being optimized for coal-based power generation are the integrated gasification combined cycle (IGCC) and the gasifier/molten carbonate fuel cell (MCFC) systems. Methods to remove hydrogen sulfide from the product gas at elevated temperatures will provide the highest possible thermal efficiency for these systems. A high-temperature desulfurization system also eliminates the need for costly heat exchanger systems to cool coal-derived gas to the required by low-temperature scrubbing processes, reheating of the clean coal-derived gases before they are injected into a combustor/turbine component, and treatment of the condensate formed during gas cooling.

A major part of the research on high-temperature desulfurization of coal-derived gases has been directed to the use of mixed-metal oxide sorbents, such as zinc ferrite, because of their ability to capture a large fraction of sulfur species in the coal gas and to be regenerated in multiple cycles of absorption and regeneration. However, quantitative evaluations of their performance during multicycle operation have shown that a gradual physical and chemical deterioration of the sorbent takes place. The sorbent's mechanical strength and its chemical reactivity for sulfur capture are strongly affected by the gasifier operating conditions.

Zinc ferrite is currently the leading candidate to serve as a sulfur removal agent in the IGCC systems. It has been demonstrated that this material can remove hydrogen sulfide from a reducing gas to levels of 10 ppmv or less at reasonable rates of reaction. GE has developed a patented moving-bed coal gas desulfurization system that has been shown to achieve a reduction in complexity and cost in a simplified IGCC system relative to conventional IGCC configurations (Cook et al., 1988). In moving-bed systems with long-term cyclic operation, the movement of pelletized sorbent requires that the sorbent have a higher degree of attrition resistance than in fixed-bed operations. In moving-bed and fixed-bed systems, chemical reactivity and physical strength of the sorbent are both important. For a constant sorbent quality, these two properties tend to vary inversely.

The moving-bed configuration offers many advantages over the fixed-bed cleanup system by minimizing sulfate formation during regeneration, minimizing accumulation of fines during sulfidation, utilization of full sorbent capacity, provision of continuous steady-state operation, and production of a high concentration sulfur dioxide tail gas stream. In this paper, results of new zinc ferrite formulations having enhanced mechanical strength over the Baseline formulation for the moving-bed application will be discussed.

2. - EXPERIMENTAL PROCEDURE

2.1 - Materials

The objective of sorbent preparation is to fabricate various zinc ferrite formulations with enhanced chemical and mechanical properties relative to the DOE-selected Baseline formulation, known as T-2465. This Baseline formulation is a cylindrical extrudate that contains 2% bentonite binder.

Several zinc ferrite formulations were prepared by United Catalysts, Inc. (UCI) and their properties are presented in Table 1. All formulations were fabricated as ellipsoidal, or "rounded" pellets with an average 0.64 cm major axis and aspect ratio between 1.1 and 1.3. Fabrication parameters selected for this study were: iron oxide type (catalyst and pigment grade), binder type (bentonite, calcium aluminate, Portland cement, titanium dioxide), binder content (up to 17% total binder), and calcination temperature (1550 and 1750 °F). The same composition of T-2465 was fabricated as a rounded pellet and labeled L-3404 in Table 1. T-2465M is a formulation fabricated as a 20,000 lb. batch following a double rounding procedure to densify the material even further.

Several guidelines were followed to assess sorbent performance and identify superior formulations for moving-bed systems. Among the guidelines, a formulation had to meet:

- Mechanical strength requirements:
 - Crush strength greater than 20 lb/pellet for the fresh material.
 - Attrition resistance greater than that of the DOE-selected Baseline formulation (ASTM procedure D4058-81) as a fresh material.
 - Attrition resistance greater than 94% (ASTM procedure D4058-81) at high temperatures (e.g., 1000 °F) as a fresh material.
- Single-pellet chemical reactivity requirements:
 - TGA fractional conversion greater than 0.5 (i.e., 50% conversion) in 2 hrs. at standard conditions (1022 °F, 1 atm., 3% H₂S).
 - TGA conversion greater than 70% of theoretical for fresh zinc ferrite.
- Pellet physical morphology requirements:
 - Specific pore volume in the range 0.2 to 0.3 cm³/g.
 - Mean pore diameter greater than 1000 Å.

Only three of the formulations that met these minimum requirements were selected for bench-scale reactor testing.

2.2 - Physical /Mechanical Characterization

The pore volume distributions of selected fresh and used sorbents were measured by a mercury porosimeter (Micromeritics Model 9220) with a mercury penetration capability of 60,000 psia. A number of measurements including pore volume, mean pore diameter (diameter at 50% intrusion), pellet density, and cumulative and differential pore volume distributions were made.

Formulations fabricated by UCI were tested for crush strength (i.e., dead weight load) and for attrition resistance at ambient temperature and at 1000 °F. Attrition resistance is defined as 100% minus attrition rate according to ASTM method D4058-81.

2.3 - Chemical Characterization

A thermogravimetric analyzer (Cahn 1000) capable of continuously measuring sorbent weight changes with an accuracy of 10 µg in reactive (or inert) gas environments as a function of temperature and time, was used to measure the chemical reactivity of the sorbents. The equipment and zinc ferrite reaction chemistry (which can be used to predict maximum weight changes) is described elsewhere (Wood et al., 1989). Typically, a 1.5-cycle reactivity test was conducted consisting of two sulfidations at 550 °C with an interim regeneration at 675 °C. Prior to each sulfidation, a 30-minute reduction was conducted at 550 °C. The gas compositions used for reduction, sulfidation, and regeneration are shown in Table 2. The sulfiding gas was typical of the GE air-blown fixed-bed gasifier except for H₂S. The abnormally high level

of H_2S , as opposed to a normal 0.5% in the sulfiding gas, was to enable a 1.5-cycle test to be performed in a normal 8-hour day.

Formulations meeting the minimum requirements described in Section 2.1 were tested in a packed-bed, bench-scale reactor unit. A schematic diagram of the bench-scale reactor unit is presented in Figure 1. The bench-unit consists of three main parts: gas-handling system, reactor system, and gas-analysis instrumentation. Compressed gases from cylinders were mixed in the gas-mixing manifold to simulate compositions typical of an air-blown, fixed-bed gasifier gas and the regeneration gases of a moving-bed, hot gas cleanup system. Three reactor vessels were operated in parallel at a space velocity of 2000 hr^{-1} each. In this way, three different formulations could be tested under identical conditions of flow rate and gas composition. The three sorbent formulations selected for testing in the reactor system were: T-2465M, L-3407, and L-3404 (the Baseline sorbent). Each reactor vessel had a 2.5 in. (6.35 cm.) internal diameter and a sorbent bed 8 in. (20.3 cm.) long.

Sulfidation was carried out at 1000°F (538°C) with an artificially high H_2S concentration (1% v/v), to accelerate the testing over 10 cycles. Gas composition was the same as that in the sulfiding gas in Table 2, except for the H_2S and N_2 concentrations. The reaction was stopped when the effluent H_2S concentration, or breakthrough concentration, reached 200 ppmv. Regeneration was carried out at 1000°F first using 1 to 4% oxygen from air (balance nitrogen), while maintaining the maximum bed temperature below 1250°F , until oxygen breakthrough was approximately equal to the inlet concentration, and then the gas mixture switched to pure air with the temperature gradually increased to 1400°F (760°C) to promote thermal decomposition of sulfate. This procedure was intended to mimic the moving bed regeneration process conditions.

3. - RESULTS

3.1 - TGA

Sorbents L-3404 (1550°F), L-3406 (1550°F), L-3407 (1550°F , 1750°F), L-3409 (1550°F), T-2465M (1550°F), and L-3467B (1750°F) were selected for chemical reactivity screening by TGA. The choice was somewhat arbitrary because of similarity of the various properties and because all sorbents met the required pore volume and mean pore diameter criteria. First cycle sulfidation capacities (as a fraction of maximum theoretical capacities) after 2 hours of sulfidation are compared for these sorbents in Table 3. For all sorbents we have assumed bentonite to be inert, ZnO to convert to ZnS via $\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$, Fe_2O_3 to convert to FeS via $\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow 2\text{FeS} + 3\text{H}_2\text{O}$ and CaAl_2O_4 to convert to CaS via $\text{CaAl}_2\text{O}_4 + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$. These reactions were used to obtain the maximum potential weight gain while fractional conversion over 2 hours was calculated by dividing the actual weight gain by the maximum potential weight gain.

All sorbents met the criteria for 70% conversion over unlimited time (defined as 8 hours maximum). However, the sorbents L-3409 and L-3467B failed to meet the 50% utilization criteria over 2 hours. Among the other sorbents, L-3406 with the pigment grade iron oxide was good in attrition resistance but was relatively unreactive. This sorbent, although not selected initially for bench-scale testing, may be used at a later date. L-3404 and its denser twin T-2465M were selected based on TGA studies. Among the L-3407 formulations, the significantly higher reactivity of the 1750°F sorbent cannot be explained readily. In any event, since the attrition properties of the two L-3407 sorbents were not significantly different, L-3407 (1750°F) was recommended for further bench-scale testing.

3.2 - Mechanical Characterization

Crush strength, attrition resistance, and mercury porosimetry measurements were conducted on fresh sorbents, on samples tested on the TGA, and on samples extracted from the bench-scale unit after multiple absorption-regeneration cycles.

The results of crush strength and attrition resistance of fresh sorbents at ambient temperature and at 1000°F are given in Table 1 and in Figure 2. Several sorbents in Table 1 exhibited low and nearly equivalent

L-3404, both containing 2% binder, is a result of differences in mean pore diameter, with T-2465M exhibiting a lower value. It is evident that the mean pore diameter, closely describing the pore volume distribution, is an important parameter for the prediction of bed reactivity when differences in other sorbent properties are not significant.

As shown in the upper x-axis scale of Figure 3, the dimensionless time provides a measure of the overall sorbent bed utilization (in terms of sulfur capture) relative to that at the calculated bed saturation time (from H_2S flow rate and mass of zinc ferrite in the bed). At the 200 ppmv H_2S breakthrough time, bed utilization between 5%-11% for L-3407 and between 20%-28% for T-2465M can be calculated. The sorbent utilization for the formulations tested is expected to be higher for commercial systems where much larger reactor beds are employed and the smaller ratio of pellet diameter to reactor diameter minimizes potential gas bypassing or channeling.

Zinc ferrite sorbents with higher bed utilization, typically 40%, have been manufactured in the past but at the expense of being weaker or softer and, hence, less suitable for long-term operation in moving-bed systems. L-3404, the Baseline formulation, has the same chemical composition of previous DOE-tested sorbents, differing in the fabrication procedure (rounding versus cylindrical extrusion).

4. - CONCLUSIONS

Based on the proposed program screening procedure, three formulations, L-3407, T-2465M, and L-3404 were selected as potential candidates for bench-scale testing and determination of enhanced formulations suitable for moving-bed applications. All formulations tested met the criteria for 70% conversion over unlimited time and suitable pellet morphology (i.e., pore volume and mean pore diameter). However, several formulations failed the criteria for 50% conversion in 2 hrs., attrition resistance, and crush strength. Pore volumes measured by mercury porosimetry correlated well with degree of sulfidation for fresh samples in TGA tests but not for cycled samples extracted from the bench-scale unit. It is speculated that the discrepancy is due to extensive thermal cycling, incomplete regeneration of calcium aluminate binder, and residual sulfate in the sorbent. Attrition resistance was somewhat higher for all fresh formulations at 1000 °F than at ambient temperature.

Bench-scale tests showed that prebreakthrough H_2S concentrations in the effluent gas are low enough for use of the sorbents in high-temperature desulfurization of coal gas, with differences in breakthrough times explained by differences in binder content and mean pore diameter of the materials. Sorbent bed capacities were below 30% of theoretical at the 200 ppmv breakthrough level and were lower than those measured in the past for weaker formulations. A significant decrease in attrition resistance was measured in the L-3407 sorbent, from 96 to 65%, while the observed crush strength was similar to that of fresh material after 10 cycles of bench-scale testing. Thus far, the three rounded formulations (L-3407, T-2465M, and L-3404) tested in the bench-scale unit appear promising for future moving-bed applications. All three rounded formulations have shown enhanced mechanical properties over the DOE-selected T-2465 Baseline formulation while maintaining adequate chemical reactivity for the moving-bed system.

5. - REFERENCES

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Woods, M.C., Leese, K.E., Gangwal, S.K., Harrison, D.P., and Jothimurugesan, K., "Reaction Kinetics and Simulation Models for Novel High-Temperature Desulfurization Sorbents," DOE/MC/24160-2671 (DE89000950), February 1989.

Table 1 - Properties of Zinc Ferrite Formulations*

Formul.	Oxide Content (%)	Binder Content (%)	Calcination Temp. (°F)	Density (lb/ft ³)	Crush Strength (lb/pellet)	Attrition Resistance (%)	Pore Vol. (cm ³ /g)	Mean Pore Diam. (Å)
L-3404	33.1 ZnO	2.0 Bentonite	1550	85.0	21	91.0	0.25	2185
	64.9 UCI Fe ₂ O ₃		1750	89.5	21	90.0	0.25	3040
L-3405	32.1 ZnO	5.0 Bentonite	1550	86.0	16	94.0	0.25	2060
	62.9 UCI Fe ₂ O ₃		1750	85.0	18.5	94.5	0.20	2330
L-3406	33.1 ZnO	2.0 Bentonite	1550	88.0	28.5	96.0	0.19	2190
	64.9 Mobay Fe ₂ O ₃		1750	90.5	27.0	95.5	0.24	2330
L-3407	28.7 ZnO	3.0 Bentonite	1550	86.5	29.0	95.0	0.24	1095
	56.3 UCI Fe ₂ O ₃		1750	86.5	20.0	96.0	0.31	3180
L-3407A	28.7 ZnO	3.0 Bentonite	1550	76.0	17.0	93.0	0.3	2185
	56.3 UCI Fe ₂ O ₃		1750	75.0	19.0	95.0	0.25	3180
L-3408	28.7 ZnO	3.0 Bentonite	1550	74.2	19.5	88.0	0.25	3180
	56.3 UCI Fe ₂ O ₃		1750	78.4	14.0	91.0	0.31	3040
L-3409	27.0 ZnO	3.0 Bentonite	1550	90.5	42	92.0	0.23	1165
	53.0 UCI Fe ₂ O ₃		1750	85.5	48	92.0	0.19	1630
L-3467A	28.7 ZnO	2.0 Bentonite	1750	90.0	35	88.0	0.20	2500
	54.9 UCI Fe ₂ O ₃							
L-3467B	28.7 ZnO	2.0 Bentonite	1750	75.0	30	90.0	0.32	3180
	54.9 UCI Fe ₂ O ₃							
T-2465M	34.7 ZnO	2.0 Bentonite	1550	89.6	22.5	95.4	0.20	1958
	64.0 UCI Fe ₂ O ₃							

* As provided by the manufacturer United Catalysts, Inc.

Table 2 - Gas Compositions (Volume %) for TGA tests

	Reducing Gas	Sulfiding Gas	Regeneration Gas
H ₂	15.0	15.0	-
CO	8.0	8.0	-
CO ₂	11.0	11.0	-
H ₂ S	-	3.0	-
H ₂ O	30.0	30.0	-
N ₂	36.0	33.0	96.0
O ₂	-	-	4.0

Table 3 - Comparison of Sorbent TGA Reactivity
Sorbent Maximum Sulfur Capacity (lbs/100 lbs) Fractional Conversion after 2-hour Sulfidation

L-3404 (1550 °F)	39.1	0.71
L-3406 (1550 °F)	39.1	0.57
L-3407 (1550 °F)	36.4	0.60
L-3407 (1750 °F)	36.4	0.77
L-3409 (1550 °F)	35.0	0.45
L-3467B (1750 °F)	36.2	0.49
T-2465M (1550 °F)	39.1	0.61

Sorbent	Table 4. – Pore Volume of Sorbents Tested on TGA			
	Fresh Pore Volume (cc/g)	Sulfided Pore Volume (cc/g)	% Sulfidation (–)	Oxidatively Regenerated Pore Volume (cc/g)
L-3404 (1550 °F)	0.25	0.13	81.4	0.24
L-3407 (1750 °F)	0.25	0.14	97.4	0.20
T-2465M (1550 °F)	0.20	0.11	100	NA

Table 5. – Physical/Mechanical Characterization of L-3407 (1750 °F) After 10 Cycles of Bench-Scale Testing				
Sample	Pore Volume (cc/g)	Mean Pore Diameter (Å)	Crush Strength (lb/pellet)	Attrition Resistance Ambient Temp. (%)
Sulfided:				
Gas Inlet	0.2173	2283	16.00	70.83
Midsection	0.2176	2004	24.93	78.25
Gas outlet	0.2130	2416	22.93	85.30
Regenerated:				
Gas Inlet	0.2107	2221	18.63	65.02
Midsection	0.2036	1795	22.17	70.04
Gas Outlet	0.2318	2440	24.87	73.43
Fresh	0.25	2126	20.0	96.0

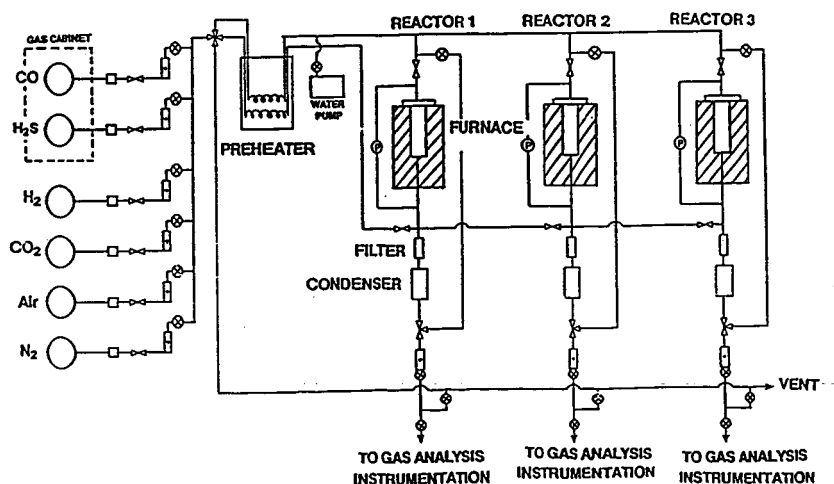


Figure 1. – Schematic Diagram of the Bench-Scale Reactor Unit

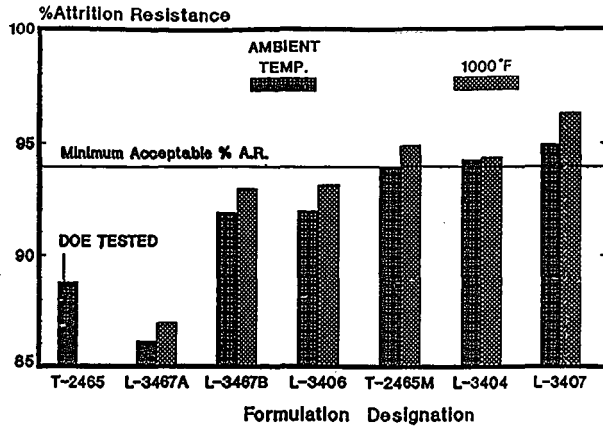


Figure 2. - Attrition Resistance Tests at 1000 °F and Ambient Temperature

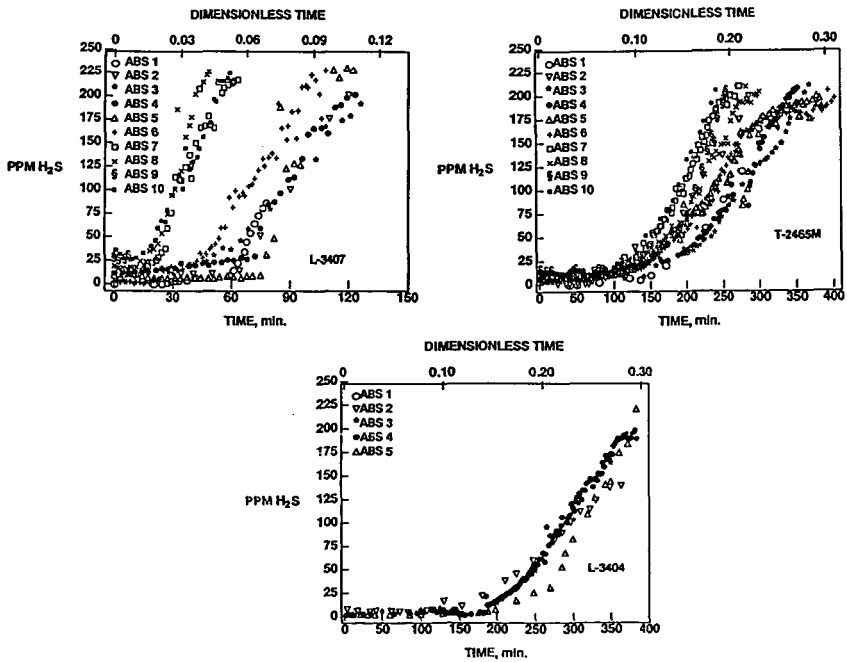


Figure 3. - Breakthrough curves for L-3407, T-2465M, and L-3404